



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US82/00473</p> <p>(22) International Filing Date: 15 April 1982 (15.04.82)</p> <p>(31) Priority Application Number: 278,253</p> <p>(32) Priority Date: 29 June 1981 (29.06.81)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: ABBOTT LABORATORIES [US/US]; 14th Street &amp; Sheridan Road, North Chicago, IL 60064 (US).</p> <p>(72) Inventors: ZOMORODI, Mostafa ; 32 Washington Blvd., Apt. 203, Mundelein, IL 60060 (US). TRIEBER, Alan, Jay ; 402 N. Greenbay Road, Apt. 116, Waukegan, IL 60085 (US).</p> <p>(74) Agent: BEISER, Robert, S.; 14th Street &amp; Sheridan Road, North Chicago, IL 60064 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p><b>Published</b>  <i>With international search report.</i>  <i>With amended claims.</i></p>
<p>(54) Title: CLEAR, AUTOCLAVABLE THERMOPLASTIC FORMULATION FOR MEDICAL LIQUID CONTAINERS</p> <p>(57) Abstract</p> <p>A clear, flexible, thermoplastic material capable of being processed into hollow shapes by conventional thermoplastic processing methods and subsequently autoclaved, comprises three components; from about 40 to 70 % by weight of a polyolefin consisting essentially of polypropylene, admixed with from about 5 to 40 % by weight of a polymer selected from the group consisting of ethylene loweralkyl acrylate; and from about 5 to 40 % by weight of a thermoplastic elastomer composition selected from the group consisting of a block copolymer consisting essentially of ethylene butylene and having terminal polystyrene units, a block copolymer consisting essentially of butadiene styrene and having terminal polystyrene units, an olefin elastomer of the ethylene propylene type, and butyl rubber (polybutadiene isoprene). The above material is particularly desirable for manufacturing medical liquid containers such as autoclavable, flexible, collapsible, intravenous solution containers.</p>		

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CLEAR, AUTOCLAVABLE THERMOPLASTIC FORMULATION FOR MEDICAL LIQUID CONTAINERS

Background of Invention

The present application relates generally to medical plastic formulations and particularly to medical liquid containers such as flexible, collapsible, intravenous solution containers. The materials disclosed exhibit the particular advantages of being essentially transparent, soft and flexible, essentially free of extractables, and able to resist high temperatures present in autoclaving.

Various materials have been utilized for intravenous solution containers in the past. In particular, U.S. Patent No. 4,140,162 discloses a formulation for medical liquid containers containing both polypropylene and a block copolymer. A third ingredient disclosed comprises polyethylene or polyethylene vinyl acetate. The present invention is distinguished from the '162 patent by the use of ethylene methyl acrylate, which is lower in cost and provides more desirable physical properties such as improved thermal stability and a wider range of processing temperatures. Other formulations of block copolymers which include polypropylene may be found in U.S. Patent No. 3,792,124. These formulations are not suitable for flexible medical liquid containers, however, in that they are ionic, which would alter the solutions contained therein.

Summary of the Invention

In accordance with this invention, a clear, flexible, thermoplastic material is provided, capable of being processed into hollow shapes by conventional plastic processing methods and subsequently autoclaved. The material comprises: (A) from about 40 to 70% by weight of a polyolefin, usually polypropylene admixed with (B) from about 5 to 40% by weight of an ethylene loweralkyl acrylate; and (C) from about 5 to 40% by weight of one of several block copolymers: ethylene butylene having terminal polystyrene units, butadiene styrene having terminal polystyrene units, an olefin elastomer of the



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ethylene propylene type, or butyl rubber (polybutadiene isoprene).

Ingredient (A) as described above is a polyolefin consisting essentially of polypropylene units.

5 Many commercial varieties of polypropylene contain small amounts of ethylene units. This does not make a major impact on the properties of the propylene material.

10 Ingredient (B) generally comprises ethylene methyl acrylate (EMA) and is commercially available from Gulf Oil Chemicals Co., Orange, Texas, under the numbers 2205 and 2255. EMA is a random copolymer consisting of a polyethylene backbone with methyl acrylate side branches. Gulf's present commercial product contains approximately 20% by weight of methyl acrylate. EMA's 15 distinguishing properties include a low melt temperature and corresponding easy heat sealability, as well as good thermal stability in the range of 600 to 630° F., and "rubbery" mechanical properties, including low stiffness, high elongation, clarity and high impact 20 strength. A comparison of ethylene methyl acrylate to ethylene vinyl acetate may be seen in the following Table I:

Table I

		<u>EMA</u>	<u>EVA</u>
25	Processing Range, F	300-620	450 Max
	Thermal Stability	Excellent	Poor
	Corrosive Possibility	No	Yes
	Pellets Require		
	Protection from Moisture		
30	During Storage	No	No
	Moisture Barrier	Fair	Fair
	Adhesion to Substrates:		
	Paper	Excellent	Excellent-Good
	OPP	Excellent	Poor
35	Cellophane (PVDC-Coated)	Excellent	Poor
	Aluminum Foil (Unprimed)	Poor	Poor
	Price, \$/lb.	59-1/2	41-1/2-61-1/2
	\$/cu. in.	2	1.4-2.0



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The general mechanical properties of EMA may be found in Table II below.

Table II

<u>Property Comparison of EMA to LDPE</u>			
	<u>EMA</u>	<u>LDPE</u>	
5	Melt Index	2.4	2
	Density, gm/cc	0.942	0.917
	Vicat Softening		
	Point, F.	138	194
10	Tensile Str. psi	1620	1850
	Elongation, %	720	650
	Hardness, Shore D	35	46
	Flex, stiffness, psi	4000	18,500
	Stress Crack Resist.	No	90%
15	(Hostapal, 122 F)	Failures	Failures
	Dielectric Constant		
	@ 100 kHz	3.1	2.3
	Dissipation Factor		
	@ 100 KHz	0.015	0.0002
20	Low-Temp. Brittleness to -105F	No	10%
		Failures	Failures
	Price, \$/lb.	59-1/2	43-1/2
		\$/cu. in.	2
			1.4

As shown in Table II, the most notable property changes brought about by the copolymerization of ethylene with methyl acrylate are: depression of melting point, significant reduction in flexural modulus, and improvement in stress crack resistance. A key attribute of EMA resin, compared with other copolymers of low density polyethylene is EMA's great thermal stability. EMA can be processed at very high temperatures; up to 600 to 630°F. without polymer breakdown and/or chain cission. Some of the other low density polyethylene copolymers, like EVA, when mixed with high temperature-resistant plastics such as polypropylene and high density polyethylene and heated in excess of 450°F. begin to break down and liberate acids that attack metal surfaces of extrusion equipment.



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Although EMA is the preferred embodiment of element B of the material, other loweralkyl ethylene acrylates may be utilized such as ethylene ethyl acrylate and ethylene butyl acrylate, with similar results.

5 "Loweralkyl" is defined as an alkyl group having 1-5 carbon atoms, such as ethyl, methyl, butyl, etc.

The third element (C) of this novel plastic material comprises from about 5 to 40% by weight of a thermoplastic composition; usually a block copolymer

10 of ethylene butylene having terminal polystyrene units.

Ethylene butylene block copolymers having terminal polystyrene units are commercially available under the trademark Kraton G<sup>®</sup> from the Shell Chemical Co. Other rubbery block copolymers such as butadiene styrene hav-

15 ing terminal polystyrene units may also be utilized.

For example, the impermeable polymeric compositions disclosed in U.S. Patent 3,686,364 assigned to Polymer Corporation Limited, hereby incorporated by reference, discloses a series of butadiene styrene block copolymers

20 useful as the third element in the present application.

Similarly, the block copolymers disclosed in U.S. Patent 3,865,776 assigned to Shell Oil Company, hereby incorporated by reference, may also be utilized. Similarly,

U.S. Patent 3,970,719 assigned to Philips Petroleum

25 Company discloses block copolymers wherein alpha olefins and/or mixtures of alpha olefins are manufactured.

These are sold under the trademark Solprene 406, 411, 414 and 475 and may also be utilized. Ethylene propylene dienemonomer, available from Exxon as Vistalon #721,

30 #404, #457, #714, #707 or #719, or ethylene propylene dienemonomer elastomer, available from Heisler Corporation under the number HC-5214, may also be used as the third ingredient of the material. Polyisobutylene elastomers sold by Exxon as LM Vistanex, Vistanex MML-80, 100 and

35 120 and isobutylene isoprene copolymers such as Exxon Butyl 077 and butyl rubber, from Polysar of Canada, may also be utilized as the third ingredient.



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The following Table III discloses a series of examples of the above listed material, showing in particular, the proportionate percentages, by weight, of elements A, B and C.

5

Table III

Preferred Embodiments

		PP	EMA	EEA	KRATON
	MATZ 10D	90%	10%		
			(2205)		
10			70%		30%
	MATZ 7D	80%	20%		
			(2255)		
			70%		30%
	MZO3-3	70%		30%	
15			70%		30%

In a preferred embodiment, 10% ethylene methyl acrylate was mixed with 90% polypropylene. The resulting combination was then mixed in a proportion of 70% EMA polypropylene to 30% element C. The resulting material exhibited the following properties, as seen in Table IV.



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Table IV

Injection Molded Test Bars		Control	Autoclaved	Irradiated	Autoclaved	Irradiated and Autoclaved
Tensile (psi)	2006	2041	1947	1947	1935	1971
Elongation (%)	490	233	707	273	473	177
100% Modulus (psi)	1909	2228	1853	2159	1948	2112
Yield (psi)	2066	2228	2041	2230	2065	2305
Workiness (1.1D-F in/in <sup>3</sup> )	9976	4973	14097	5702	9460	3784
<u>MATR 71</u>						
Tensile (psi)	1042	1812	1818	1795	1947	1842
Elongation (%)	520	440	587	367	600	303
100% Modulus (psi)	1713	1883	1648	1817	1795	1842
Yield (psi)	1653	1787	1653	1748	1724	1760
Workiness (1.1D-F in/in <sup>3</sup> )	9017	7918	10187	6501	11013	6898
<u>M203-3</u>						
Tensile (psi)	1994	1842	1830	1760	1771	1842
Elongation (%)	637	360	663	533	540	520
100% Modulus (psi)	1560	1807	1490	1690	1467	1713
Yield (psi)	1525	1666	1525	1455	1408	1678
Workiness (1.1D-F in/in <sup>3</sup> )	12088	6314	11122	8568	8583	9152

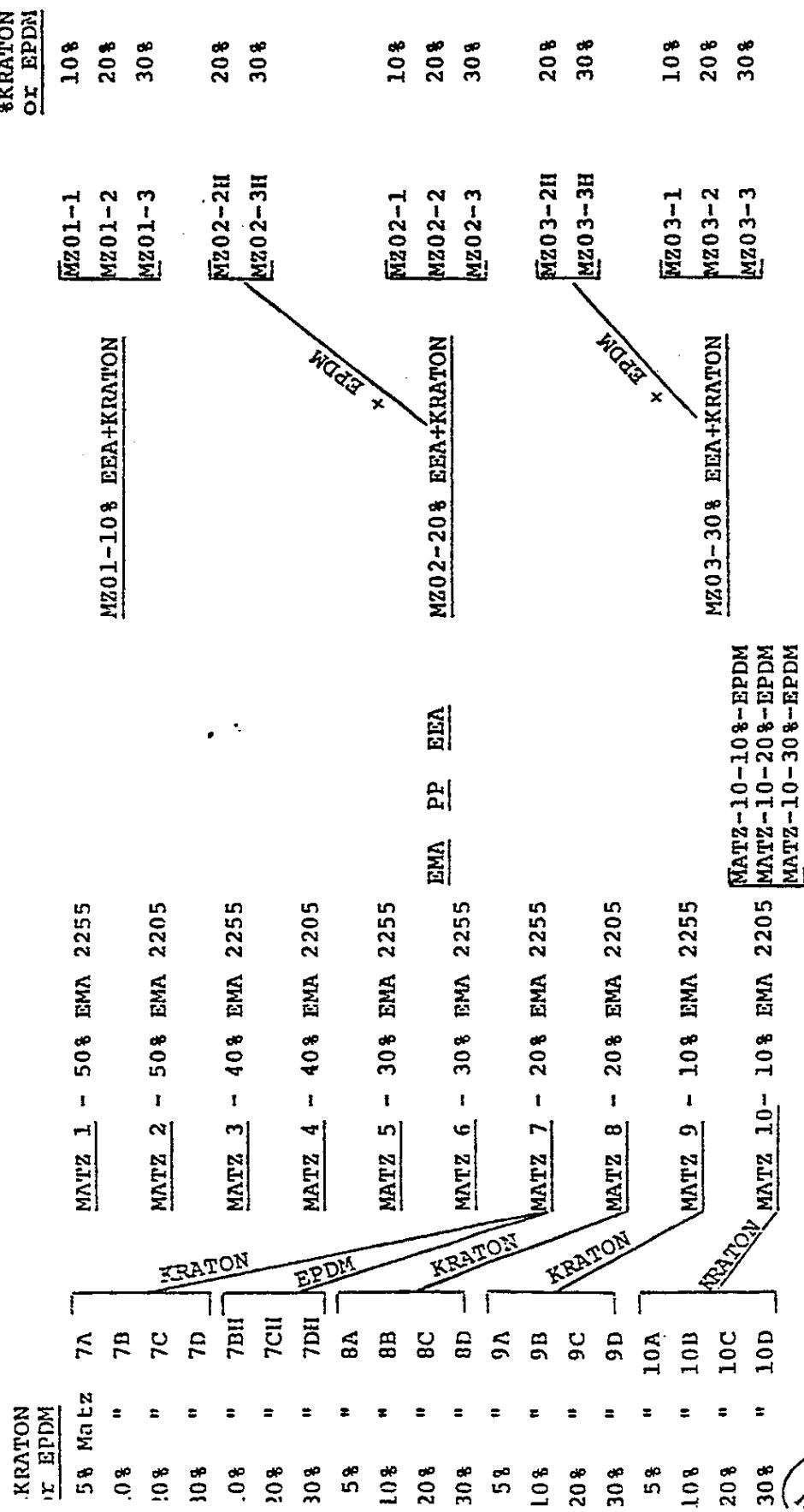


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In addition, the resulting formulation was found to be highly suitable for sheet extrusion, injection molding or blow molding into flexible, transparent, autoclavable intravenous solution containers. In particular, the resulting container was found to be of sufficient strength to withstand heavy impact during shipment and use, while at the same time being sufficiently flexible to collapse easily during drainage of intravenous solution from the container.

The following examples further illustrate specific embodiments of the invention.





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Example 1

A block copolymer having thermoplastic rubber characteristics consisting essentially of a rubbery olefin polymer of generally equal proportions of ethylene and butylene units in terminal blocks of polystyrene was added to a rotational mixer in the amount of 40% by weight with 10% by weight of a blend of 90% polypropylene and 10% EMA. The block copolymer used was Kraton 2705 sold by the Shell Chemical Company. Mechanical properties of Kraton 2705 are as follows:

Hardness, shore A	52
Tensile properties, ASTM D-412	
Tensile strength, psi	1650
Elongation at break	800
Modulus at 100% extension, psi	200
Set after break, %	55
Tear strength, pli (ASTM D-624)	130
Compression set at 70°C, % (ASTM D-395)	32
Yerzley resilience, % (ASTM D-945)	75
Specific gravity	0.90

The ingredients were premixed in the rotational mixer and then introduced into an extruder for extrusion into a rod. The rods were then chopped into smaller pellet sized pieces. The chopped pellets were utilized in the commercially available blow molding apparatus, specifically a continuous extrusion machine, with a secondary blow station manufactured by Romellog Fellbach of Oeffingen. The material was found to be successfully fabricated into a transparent, flexible, collapsible intravenous solution container which was autoclavable under a typical sterilizing cycle without an distortion.

Example 2

The above listed percentages were duplicated utilizing as element C of the composition, a different block copolymer, said block copolymer being either a linear or a branched block copolymer having at least two



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polymer blocks A and at least one polymer block B, each polymer block A being selected from the group consisting of monoalkenyl arine polymers and hydrogenated products thereof wherein no more than 25% of the arine double  
5 bonds had been reduced and polymer block B is a hydro-  
genated polymer block of a C<sub>4</sub>-5 conjugated diene polymer  
wherein at least about 30% of the aliphatic unsaturation  
has been reduced by hydrogenation. Specifically, each  
10 polystyrene block has an average molecular weight be-  
tween about 2,000 and 50,000 and the hydrogenated poly-  
butadiene block has an average molecular weight between  
about 20,000 and 300,000.

Example 3

15 A block copolymer of general form polyalpha-methyl-styrene-polybutadine-polyethylmethyl styrene  
(hereinafter referred to as alpha-beta-alpha block co-  
polymer) was prepared and blended with uncured butyl  
rubber. The alpha-beta-alpha block copolymer had an  
alpha methyl styrene content of approximately 35% weight  
20 and a molecular weight of about 60,000. Three separate  
blends were prepared using 30, 40 and 50 parts by weight  
of butyl rubber respectively with 100 parts by weight  
of alpha-beta-alpha block copolymer. The blending was  
carried out on a micromil, the mil rolls were at  
25 elevated temperatures in the range of about 130°C. to  
about 150°C. The resulting blends were then admixed  
with components A and B as previously described.

Example 4

30 In this Example, the same percentages of ele-  
ments A and B of the composition are disclosed in Example  
2. Element C comprises 10% by weight of a thermoplastic  
composition comprising a block copolymer having at least  
two monoalkenyl arine polymer blocks and at least one  
substantially completely hydrogenated diene polymer  
35 block. For example, polymer block A is a block copolymer  
having the structure polystyrene-completely hydrogenated



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polybutadiene-polystyrene with block molecular weights of 25,000-100,000-25,000. An alternative formulation is a block copolymer of the same structure and block identity but having block molecular weights of 10,000-50,000-  
5 10,000.

Example 5

A block copolymer of general form polyethyl-methyl styrene polybutadiene polyethyl methyl styrene was prepared with different quantities of uncured butyl rubber. The alpha-beta-alpha block copolymer had an alpha methyl styrene content of approximately 35 percent by weight and a molecular weight of about 60,000. The nonterminal elastomer block may be polybutadiene, or polybutadiene and butyl rubber. The resulting block  
10 15 copolymer was then admixed with components A and B.

Example 6

Other specific aliphatic olefins, aromatic olefins and/or mixtures thereof may be selected from the following list and utilized according to the teachings herein:

TPR thermoplastic rubber 1600, Uniroyal, Inc.  
Naugatuk, Connecticut;  
Combinations of isotactic polypropylene and ethylene propylene rubber;  
25 TPR thermoplastic rubber 1900, Uniroyal, Inc.,  
Naugatuk, Connecticut;

As in an additional ingredient, from .25 to .5% of a nucleating agent such as sodium benzoate or millad 3900 polyolefin clarifies both manufactured by Milliken Corp., may be added to the above listed formulations to improve clarity.

The foregoing description and drawings merely explain and illustrate the invention, and the invention is not so limited thereto, except insofar as the appended claims are limited to those skilled in the art who have the disclosure before them and are able to make modifications and variations therein without departing from the scope of the invention.



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WHAT IS CLAIMED IS:

1. A clear, flexible thermoplastic material capable of being processed into hollow shapes by conventional plastic processing methods and subsequently autoclaved comprising:

5 (a) from about 40 - 70% by weight of a polyolefin consisting essentially of polypropylene, admixed with,

(b) from about 5 - 40% by weight of ethylene loweralkyl acrylate polymers, and

10 (c) from about 5 to 40% by weight of a thermoplastic elastomer composition selected from the group consisting of:

an ethylene butylene block copolymer having terminal polystyrene units,

15 a butadiene styrene block copolymer having terminal polystyrene units,

an olefin elastomer of the ethylene propylene type; and

butyl rubber.

2. A clear, flexible thermoplastic material capable of being blow molded and autoclaved comprising:

(a) from about 40 to 70% by weight of a polyolefin consisting essentially of propylene admixed with,

5 (b) from about 5 to 40% by weight of a polymer selected from the group consisting of ethylene loweralkyl acrylates, and

10 (c) from about 5 to 40% by weight of a thermoplastic elastomer selected from the group consisting of polyolefin elastomers, polyester elastomers, block copolymers of styrene and butadiene or isoprene or butadiene isoprene, and block copolymers of styrene and ethylene or butylene or ethylene butylene.



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3. The thermoplastic formulation as disclosed in Claim 1 wherein said ethylene butylene block copolymer has a central block comprising 50 to 85% by weight of the copolymer molecule of a rubbery olefin polymer of generally equal proportions of ethylene and butylene units; and terminal blocks of polystyrene.

4. The thermoplastic formulation as disclosed in Claim 1 wherein said thermoplastic composition comprises:

a block copolymer having at least two polymer blocks A and at least one polymer block B, each polymer block A being selected from the group consisting of monoalkenyl arene polymers and hydrogenated products thereof wherein no more than 25% of the arene double bonds have been reduced and polymer block B is a hydrogenated polymer block of a C 4-5 conjugated diene polymer wherein at least about 30% of the aliphatic unsaturation has been reduced by hydrogenation.

5. The thermoplastic formulation as disclosed in Claim 1 and wherein said block copolymer has thermoplastic terminal blocks selected from polystyrene and polyalphamethyl styrene and the nonterminal elastomer block is a polymer of a conjugated diolefinic hydrocarbon and a polymer comprising isobutylene and butyl rubber.

6. The thermoplastic formulation as disclosed in Claim 1 wherein said block copolymer has at least two monoalkenylarene polymer blocks and at least one substantially completely hydrogenated diene polymer block.

7. The thermoplastic formulation as disclosed in Claim 3 wherein said polyolefin (a) and said polymer (b) are mechanically combined in a mixture of approximately 90% by weight polyolefin and 10% by weight polymer, said mixture then being mechanically combined with said thermoplastic composition in a ratio of approximately 70% by weight polyolefin/polymer mixture to approximately 30% by weight thermoplastic composition.



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8. The thermoplastic formulation as disclosed in Claim 1 wherein said ethylene loweralkyl acrylate is selected from the group consisting of ethylene methyl acrylate, and said polyolefin and said polymer are mechanically combined in a mixture of approximately 90% by weight polyolefin and 10% by weight ethylene methyl acrylate, said mixture then being mechanically combined with ethylene propylene dienemonomer elastomer in a ratio of approximately 70% by weight polyolefin/ethylene methyl acrylate to approximately 30% ethylene propylene dimonomer elastomer.

9. The thermoplastic formulation as disclosed in Claim 5 wherein said thermoplastic elastomer block copolymer is polyalphamethylstyrene-polydiolefins-polyalphamethylstyrene block copolymer containing about 30-35 percent by weight of alphamethylstyrene.

10. The thermoplastic formulation as disclosed in Claim 5 wherein said nonelastomeric block is polybutadiene.

11. The composition of Claim 5 wherein said isobutylene polymer is butyl rubber.

12. The thermoplastic composition as disclosed in Claim 6 wherein said block copolymer has the structure polystyrene hydrogenated polybutadiene polystyrene.

13. A clear, flexible, collapsible container capable of being blow molded and autoclaved, made from the thermoplastic material disclosed in Claim 1 or 2.

14. A clear, flexible, collapsible medical liquid container capable of being blow molded and autoclaved, made from the thermoplastic material disclosed in Claim 1 or 2.

15. The thermoplastic formulation as disclosed in Claim 1 or 2 wherein a nucleating agent selected from the group consisting of sodium benzoate is added in a concentration of .25 to .5% by weight thereby markedly improving the clarity of said thermoplastic formulation.



**AMENDED CLAIMS**  
(received by the International Bureau on 1st November 1982 (01.11.82))

(amended) 1. A clear, flexible thermoplastic material capable of being processed into hollow shapes by conventional plastic processing methods and subsequently autoclaved comprising:

(a) from about 40 - 70% by weight of a polyolefin consisting essentially of polypropylene, mixed with,

(b) from about 5 - 40% by weight of ethylene loweralkyl acrylate polymers, and

(c) from about 5 to 40% by weight of a thermoplastic elastomer composition selected from the group consisting of:

an ethylene butylene block copolymer having terminal polystyrene units, and

a butadiene styrene block copolymer having terminal polystyrene units[,

an olefin elastomer of the ethylene propylene type; and

butyl rubber].

(amended) 2. A clear, flexible thermoplastic material capable of being blow molded and autoclaved comprising:

(a) from about 40 to 70% by weight of a polyolefin consisting essentially of propylene admixed with,

(b) from about 5 to 40% by weight of a polymer selected from the group consisting of ethylene loweralkyl acrylates, and

(c) from about 5 to 40% by weight of a thermoplastic elastomer selected from the group consisting of [polyolefin elastomers, polyester elastomers] block copolymers of styrene and butadiene or isoprene or butadiene isoprene, and block copolymers of styrene and ethylene or butylene or ethylene butylene.



3. The thermoplastic formulation as disclosed in Claim 1 wherein said ethylene butylene block copolymer has a central block comprising 50 to 85% by weight of the copolymer molecule of a rubbery olefin polymer of generally equal proportions of ethylene and butylene units; and terminal blocks of polystyrene.

4. The thermoplastic formulation as disclosed in Claim 1 wherein said thermoplastic composition comprises:

5 a block copolymer having at least two polymer blocks A and at least one polymer block B, each polymer block A being selected from the group consisting of monoalkenyl arene polymers and hydrogenated products thereof wherein no more than 25% of the arene double bonds have been reduced and polymer block B is a  
10 hydrogenated polymer block of a C 4-5 conjugated diene polymer wherein at least about 30% of the aliphatic unsaturation has been reduced by hydrogenation.

5. The thermoplastic formulation as disclosed in Claim 1 and wherein said block copolymer has thermoplastic terminal blocks selected from polystyrene and polyalphamethyl styrene and the nonterminal elastomer block is a polymer of a conjugated diolefinic hydrocarbon and a polymer comprising isobutylene and butyl rubber.

6. The thermoplastic formulation as disclosed in Claim 1 wherein said block copolymer has at least two monoalkenylarene polymer blocks and at least one substantially completely hydrogenated diene polymer block.

7. The thermoplastic formulation as disclosed in Claim 3 wherein said polyolefin (a) and said polymer (b) are mechanically combined in a mixture of approximately 90% by weight polyolefin and 10% by weight polymer, said mixture then being mechanically combined with said thermoplastic composition in a ratio of approximately 70% by weight polyolefin/polymer mixture to approximately 30% by weight thermoplastic composition.

8. The thermoplastic formulation as disclosed in Claim 1 wherein said ethylene loweralkyl acrylate is selected from the group consisting of ethylene methyl acrylate, and said polyolefin and said polymer are mechanically combined in a mixture of approximately 90% by weight polyolefin and 10% by weight ethylene methyl acrylate, said mixture then being mechanically combined with ethylene propylene dienemonomer elastomer in a ratio of approximately 70% by weight polyolefin/ethylene methyl acrylate to approximately 30% ethylene propylene dienomonomer elastomer.

9. The thermoplastic formulation as disclosed in Claim 5 wherein said thermoplastic elastomer block copolymer is polyalphamethylstyrene-polydiolefins-poly-alpha-methylstyrene block copolymer containing about 30-35 percent by weight of alphamethylstyrene.

10. The thermoplastic formulation as disclosed in Claim 5 wherein said nonelastomeric block is polybutadiene.

11. The composition of Claim 5 wherein said isobutylene polymer is butyl rubber.

12. The thermoplastic composition as disclosed in Claim 6 wherein said block copolymer has the structure polystyrene hydrogenated polybutadiene polystyrene.

13. A clear, flexible, collapsible container capable of being blow molded and autoclaved, made from the thermoplastic material disclosed in Claim 1 or 2.

14. A clear, flexible, collapsible medical liquid container capable of being blow molded and autoclaved, made from the thermoplastic material disclosed in Claim 1 or 2.

15. The thermoplastic formulation as disclosed in Claim 1 or 2 wherein a nucleating agent selected from the group consisting of sodium benzoate is added in a concentration of .25 to .5% by weight thereby markedly improving the clarity of said thermoplastic formulation.



# INTERNATIONAL SEARCH REPORT

International Application No PCT/US82/00473

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC  
 INT. CL. 3 C08L 23/12, 23/08, 23/16, 23/22 53/00, 53/02, 67/02  
 US CL. 525/96, 166, 211, 227

## II. FIELDS SEARCHED

Minimum Documentation Searched 4

Classification System	Classification Symbols
U.S.	525/96, 166, 211, 227

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched 5

## III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

Category 6	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
A	US, A, 4,107,130, PUBLISHED 15 AUGUST 1978 GERGEN ET AL	1-15
A	US, A, 3,361,852, PUBLISHED 2 JANUARY 1968 BASSETT ET AL	1-3, 5-15
P, X	US, A, 4,277,578, PUBLISHED 7 JULY 1981 YOSHIMURA ET AL	1-3, 5-15

### \* Special categories of cited documents: 13

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actus: Completion of the International Search 2  
01 JULY 1982

Date of Mailing of this International Search Report 3

20 AUG 1982

International Searching Authority 1  
ISA/US

Signature of Authorized Officer 2  
CARMEN SECCURO

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 10

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers \_\_\_\_\_, because they relate to subject matter<sup>12</sup> not required to be searched by this Authority, namely:
  
2.  Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out<sup>13</sup>, specifically:

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 11

This International Searching Authority found multiple inventions in this international application as follows:

SEE FORM 206

1.  As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims of the international application.
2.  As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the international application for which fees were paid, specifically claims:
  
3.  No required additional search fees were timely paid by the applicant. Consequently, this International search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
  
4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

The additional search fees were accompanied by applicant's protest.  
 No protest accompanied the payment of additional search fees.